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# On the correlation between Moelwyn-Hughes parameter and thermo-acoustical parameters of rare earth metals and reference materials

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**Abstract :** Thermo-acoustical parameters of rare earth metals and reference materials are evaluated in terms of the coefficient of expansivity, on the assumption that the Moelwyn-Hughes Parameter is the dominant factor. The Moelwyn-Hughes parameter has been utilized to establish a simple relationship between the lattice Gruneisen parameter, Rao's acoustical parameter, Beyer's non-linearity parameter and the molecular constant. An attempt has also been made to correlate these parameters with the free volume of the molecule, the repulsive exponent and the isochoric acoustical parameter. All these parameters are interrelated with the Moelwyn-Hughes parameter only. Sharma's parameter has been found to be approximately constant in the case of the rare earth metals and reference materials.

**Keywords :** Rare earth metals, reference materials, Moelwyn-Hughes parameter, Beyer's non-linearity parameter, Gruneisen parameter, Sharma's parameter.

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## 1. Introduction

The Gruneisen parameter is an important quantity of current interest for studying the internal structure, molecular order and other thermo-acoustic parameters of liquids (Slater 1939, Warfield and Hartmann 1973, Sharma 1985) and polymers (Sharma 1982, 1983a, Reddy *et al* 1987). Many workers have studied the thermo-acoustic properties in the case of liquefied gases (Rao 1941), molten metals (Sharma 1981) and some polymers (Sharma and Reddy 1984). In the case of rare earth metals and reference materials only does the microscopic Gruneisen parameter vary from 19 to 276 (in the present study), while it is constant in the cases of liquefied gases and molten metals. This parameter, widely used in equation of

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state calculations, serves as an effective guide in determining the mechanism of ultrasonic absorption in polymers, and also in establishing a correlation with the results of phonon-phonon interaction absorption. Some mathematical relationships are also available for calculating the Gruneisen parameter. The model proposed by Sharma (1983b) have been used in the present study for calculating the Gruneisen parameter.

In the present paper, the authors aim to examine and analyse the various possible relationships between the Moelwyn-Hughes parameter, the microscopic Gruneisen parameter, Rao's acoustical parameter and Beyer's non-linearity parameter. Many other thermo-acoustic parameters are interrelated through one and only one parameter, namely the Moelwyn-Hughes parameter. Such analysis is not found so far in the literature in the case of rare earth metals and reference materials. The present study demonstrates the importance of Moelwyn-Hughes parameter in evaluating various thermo-acoustic parameters of rare earth metals and reference materials.

## 2. Theoretical

The lattice Gruneisen parameter $\Gamma$ can be defined as (Slater 1939, Dugdale and MacDonald 1953)

$$\Gamma = -(\partial \ln \nu / \partial \ln V) \tag{1}$$

$\nu$ is the anharmonicity of normal mode frequency of lattice vibrations with molar volume $V$.

For the liquid state, Moelwyn-Hughes and Rao defined the parameters as (Moelwyn-Hughes 1951, Rao 1941)

$$C_1 = (\partial \ln \beta / \partial \ln V) \tag{2}$$

$$K = -(\partial \ln U / \partial \text{ in } V) \tag{3}$$

where $\beta$ is the compressibility at absolute temperature $T$ and $U$ is the bulk sound velocity.

For polymers, Sharma (1981) related $\Gamma$, $K$ and $C_1$ as

$$\Gamma = K = (C_1 - 1)/2 \tag{4}$$

In terms of linear thermal expansivity ($\alpha$), Sharma (1981) derived the relations with the assumption that polymers as quasi-solids as

$$C_1 = [(13)/3 + (\alpha T)^{-1} + (4/3)(\alpha T)] \tag{5}$$

$$\Gamma = K = [(5/3) + (2\alpha T)^{-1} + (2/3)(\alpha T)] \tag{6}$$

The above relations are clearly known with the view of Hartmann (1979) that the anharmonicity of intermolecular potential which gives rise to a volume dependence

of normal mode frequency is also responsible for thermal expansion. So, the interrelationship between $\alpha$ and $\Gamma$ is not strange.

According to Sharma (1983a), the three dimensionless anharmonic parameters $\Gamma$, $\Gamma'$ and $\Gamma''$ are related as follows.

$$\Gamma = \Gamma' + \Gamma'' \tag{7}$$

where $\Gamma'$ and $\Gamma''$ are isothermal and isobaric Gruneisen parameters respectively. The details of the relations are described elsewhere (Sharma 1983a).

The parameter $\Gamma''$ is a negative quantity for polymers and a positive quantity for liquids (Sharma 1983b). It can be written as

$$\Gamma'' = -((X-Y)/Y) \tag{8}$$

where

$$X = [2+(\alpha T)^{-1}(-2\alpha)(\bar{V}C_1)^{-1}] \tag{9}$$

and

$$Y = -2\alpha \tag{10}$$

In the above relations $\bar{V}$ is the reduced volume, and the other symbols have their usual significance.

Recently Sharma (1983b) proposed a relation between Beyer's parameter of nonlinearity $(B/A)$, the Moelwyn-Hughes $(C_1)$ and Rao's acoustical parameters $(K)$ as

$$C_1 = (B/A)_0 + 1 = (2\Gamma + 1) \tag{11}$$

$$(B/A)_0 = C_1 - 1 \tag{12}$$

where

$$(B/A)_0 = \left(\frac{m+n+3}{3}\right) = 2K \tag{13}$$

Here $m$ and $n$ are respectively the exponents describing the magnitude of attractive and repulsive forces of the molecules. $(B/A)_0$ is the value of $(B/A)$ corresponding to the volume $V_0$.

If $m = 6$,

$$3[(B/A)_0 - 3] = n = 2[C_1 - 4] \tag{14}$$

The above relation signifies the intermolecular force through the repulsive exponent $n$ which plays a vital role in establishing a close relationship between the anharmonic and nonlinear properties.

$$K = \Gamma = [(V_a/V) - 1] \tag{15}$$

$$= [(C_1 - 1)/2] \tag{16}$$

where $V_a$ is the free volume of the molecules and V is the total volume.

Sharma (1983c, d) has introduced two dimensionless parameters, $S_0$ and $S^*$ as

$$S_0 = \delta(3+4\alpha T) = 3\delta S^* \tag{17}$$

$$S^* = [1+((4/3)\alpha T)] \tag{18}$$

where $\delta$ is the isochoric acoustical parameter and it can be computed as follows

$$\delta = -\frac{[2+(\alpha T)^{-1}(-2\alpha)(\tilde{V}^{\sigma_1})^{-1}T]}{2} \tag{19}$$

The molecular constant ($r$) can be calculated using the value of $\delta$ as follows (Sharma 1983b, 1983f)

$$r = P_i/\epsilon = (1-\delta)^{-1} \tag{20}$$

where $P_i$ and $\epsilon$ are the internal pressure and cohesive energy density.

Eqs. (4), (9), (11), (16) and (19) involve the Moelwyn-Hughes parameter $C_1$. It shows the importance of $C_1$ in evaluating various thermo-acoustic parameters. As shown below, $C_1$ can be expressed in many ways which demostrate how simply $C_1$ is related to other parameters (Reddy *et al* 1987).

$$C_1 = [(13/3)+(\alpha T)^{-1}+(4/3)(\alpha T)] \tag{21}$$

$$C_1 = 2\Gamma+1 \quad \text{or} \quad C_1 = 2K+1 \tag{22}$$

$$= (B+A)_0+1 \quad \text{or} \quad (n+12)/3 \tag{23}$$

$$= 2(V/V_a)-1 \quad \text{or} \quad 1+2[\Gamma'+\Gamma''] \tag{24}$$

$$= \log [T/\delta(2\alpha+1/T)]/\log (\tilde{V}) \tag{25}$$

and

$$\delta = (T/(\tilde{V})^{\sigma_1})[2\alpha+1/T] \tag{26}$$

$$r = \frac{1}{1-(T/(V)^{\sigma_1})[2\alpha+1/2]} \tag{27}$$

$\Gamma$, $K$, $(B/A)_0$, $n$, $(V/V_a)$, $\delta$, $(\Gamma'+\Gamma'')$ and $r$ are related directly with the Moelwyn-Hughes parameter only.

## 3. Results and discussion

Values of $\Gamma$, $C_1$, $(B/A)$, $(V_a/V)$, $\delta$, $n$ and $r$ are computed utilizing the above relations. $X$, $Y$, $S^*$ and $S_0$ are evaluated through the equations given by Sharma (1983c, d). The evaluated thermo-acoustic parameters for the rare earth metals and reference materials are presented in Tables 1 and 2. The necessary data relevent to the present work is taken from the literature (Narayana and Swamy 1978, White 1973). The present treatment has the great advantage of calculating various

**Table I.** The values of Gruneisen parameter, Moelwyn-Hughes parameter, Beyer's nonlinearity parameter, isochoric acoustical parameter, Rao's acoustical parameter, repulsive exponent, molecular constant of rare earth metals at 300 K.

| Materials | $10^{-4}K^{-1}$ | $\Gamma=K$ | $C_i$ | $B/A$ | $V_a/V$ | $X$ | $\delta$ | $\gamma$ $10^{-2}$ | $n$ | $S^*$ | $S_0$ | $r$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| La | 0.1470 | 115.04 | 231.09 | 230.096 | 0.0086 | −0.0024 | 0.3659 | −2.94 | 681.28 | 1.0058 | 1.1044 | 1.577 |
| Ce | 0.2550 | 67.03 | 135.06 | 134.06 | 0.0146 | −0.0024 | 0.3646 | −5.10 | 393.18 | 1.0102 | 1.1050 | 1.573 |
| Pr | 0.2037 | 83.49 | 167.98 | 166.98 | 0.0118 | −0.0024 | 0.3652 | −4.07 | 491.94 | 1.0081 | 1.1047 | 1.575 |
| Nd | 0.2996 | 57.33 | 115.67 | 114.67 | 0.0171 | −0.0024 | 0.3640 | −5.98 | 335.03 | 1.0119 | 1.1052 | 1.572 |
| Sm | 0.3120 | 55.09 | 111.18 | 110.18 | 0.1782 | −0.0024 | 0.3638 | −6.24 | 321.55 | 1.0124 | 1.1053 | 1.572 |
| Eu | 0.9600 | 19.04 | 39.09 | 38.09 | 0.0498 | −0.00237 | 0.3558 | −0.19 | 105.28 | 1.0380 | 1.1084 | 1.552 |
| Gd | 0.2484 | 68.76 | 138.53 | 137.53 | 0.0143 | −0.0024 | 0.3647 | −4.90 | 403.60 | 1.0099 | 1.1043 | 1.574 |
| Tb | 0.3030 | 56.67 | 114.35 | 113.35 | 0.0173 | −0.0024 | 0.3640 | −6.06 | 331.06 | 1.0121 | 1.1052 | 1.572 |
| Dy | 0.3000 | 57.22 | 115.45 | 114.45 | 0.0171 | −0.0024 | 0.3640 | −6.00 | 334.36 | 1.0120 | 1.1052 | 1.572 |
| Ho | 0.3210 | 53.59 | 108.18 | 107.18 | 0.0183 | −0.0024 | 0.3637 | −6.42 | 312.56 | 1.0120 | 1.1053 | 1.571 |
| Er | 0.3690 | 46.84 | 94.68 | 93.68 | 0.0209 | −0.0024 | 0.3631 | −7.38 | 272.04 | 1.0140 | 1.1056 | 1.570 |
| Tm | 0.3990 | 43.44 | 87.89 | 86.89 | 0.0224 | −0.0024 | 0.3627 | −7.98 | 251.67 | 1.0159 | 1.1057 | 1.569 |
| Yb | 0.7488 | 23.93 | 48.87 | 47.87 | 0.0400 | −0.0023 | 0.3580 | −1.49 | 134.63 | 1.0229 | 1.1074 | 1.558 |

**Table 2.** The values of Gruneisen parameter, Rao's acoustical parameter, Moelwyn-Hughes parameter, Bayers nonlinearity parameter, isochoric acoustical parameter, repulsive exponent, molecular constant of reference materials.

| Material | $\alpha$ $10^{-5}K^{-1}$ | $\Gamma=K$ | $C_1$ | $B/A$ | $V_a/V$ | $X$ | $\delta$ | $\gamma$ $10^{-5}$ | $n$ | $S^*$ | $S_0$ | $r$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Copper | 16.43 | 109.20 | 219.40 | 218.40 | 0.00910 | −0.00258 | 0.3658 | −3.286 | 646.22 | 1.0060 | 1.1044 | 1.5770 |
| Copper (300 K) | 16.61 | 108.03 | 217.07 | 216 07 | 0.00910 | −0.00258 | 0.3658 | −3.322 | 639.23 | 1.0060 | 1.1044 | 1.5760 |
| Ag | 18.71 | 95.84 | 192.69 | 191.69 | 0.01030 | −0.00258 | 0.3656 | −3.752 | 566.09 | 1.0070 | 1.1045 | 1.5760 |
| Al | 22.45 | 80.36 | 161.73 | 160.73 | 0.01220 | −0.00258 | 0.3651 | −4.490 | 473.21 | 1.0080 | 1.1047 | 1.3752 |
| Au | 14.05 | 127.41 | 255.83 | 254.83 | 0.00778 | −0.00259 | 0.3661 | −2.810 | 755.51 | 1.0050 | 1.1045 | 1.5777 |
| Ir | 6.42 | 276.86 | 554.73 | 553.73 | 0.00359 | −0.00258 | 0.3671 | −1.284 | 1652.20 | 1.0024 | 1.1039 | 1.5800 |
| Pd | 11.60 | 153.97 | 308.95 | 307.95 | 0.00640 | −0.00259 | 0.3664 | −2.320 | 914.86 | 1 0043 | 1.1042 | 1.5784 |
| Pt | 8.76 | 203.35 | 407.71 | 406.71 | 0.00489 | −0.00259 | 0.3668 | −1.752 | 1211.13 | 1.0033 | 1.1040 | 1.5793 |
| Rh | 8.30 | 214.53 | 430.06 | 429.06 | 0.00460 | −0.00259 | 0.3668 | −1.660 | 1278.20 | 1.0031 | 1.1040 | 1.5794 |
| MgO | 9.84 | 181.21 | 363.43 | 362.43 | 0.00540 | −0.00259 | 0.3666 | −1.968 | 1078.31 | 1.0037 | 1.1041 | 1.5789 |
| NaCl | 39.10 | 46.86 | 94.72 | 93.72 | 0.00280 | −0.00250 | 0.3631 | −7.820 | 272.16 | 1.0147 | 1.1056 | 1.5702 |
| CaFz | 18.41 | 97.63 | 196 27 | 195.27 | 0.01010 | −0.00250 | 0.3656 | −3.682 | 576.83 | 1.0069 | 1.1045 | 1.5764 |

parameters which describe the thermo-acoustic properties of polycrystalline solids employing only the expansivity data. The reference and rare earth metals are readily available in high state of purity (Narayana and Swamy 1978, White 1973) and some of the physical properties of these elements have not been determined accurately. It may be observed from Tables that $C_1$ values vary from 40 to 555 for the materials studied. The values of $X$ are negative and is found to be constant ($\sim 2.0 \times 10^{-3}$) in the present study. However, the values of $X$ vary from $1.5 \times 10^{-3}$ to $2.3 \times 10^{-3}$ in the case of polymers (Reddy *et al* 1987, Sharma 1983b). The present values of $(B/A)_0$ for these materials are different from those of fluoro-carbon fluids (Sharma 1983e), polymers and organic liquids (Reddy *et al* 1987, Sharma 1983b). The fractional free volume ($V_f/V_a$), Sharma's thermo-acoustical parameters $S_0$ and $S^*$ are also presented in the Tables 1 and 2. It may be noted that in the case of rare-earth metals and in reference materials, lanthanum and iridium have highest $\Gamma$, $C_1$, $B/A$, $n$ and $r$ because of the lowest $\alpha$ value. The higher values of $n$ in this study is due to the strong anisotropic and anharmonicity nature of the materials. This is in good agreement with the view of Soczkiewiez (1977). The isochoric acoustical parameter $\delta$ is found to be constant (0.36) in the present study. The magnitude of the $(V_a/V)$ values in these materials is very less than that for hydrocarbon liquids (Soczkiewiez 1977), polyatomic ionic liquids (Sharma and Reddy 1985) and polymers (Reddy *et al* 1987). It may be interesting to note that $S_0 \sim 1.1$, and $S^* \sim 1.0$ on the average. A careful observation of the results reveals that an approximate relationship between molecular constant ($r$) $\delta$, $S_0$ and $S^*$ i.e.

$$r \approx 4.36\delta$$

$$r \doteq S^* + 0.57 \approx S_0 + 0.47$$

holds true for rare earth metals and reference materials. The relations given above for $r$ indicates that molecular constant, Sharma's dimensionless parameters $S_0$ and $S^*$ and isochoric acoustical parameter $\delta$ are interrelated.

The relations given by eqs. (21)–(27) above have special significance in relating various thermo-acoustical parameters with a single parameter, namely, Moelwyn-Hughes parameter. These type of relations are very helpful in evaluating and understanding various properties whenever limited experimental data is available. The present treatment allows a convenient way for evaluating the microscopic Gruneisen parameter, Beyer's non-linearity parameter and other thermo-acoustic parameters through the Moelwyn-Hughes parameter, which has not, perhaps, been done so far for these materials. This offers further understanding of the significance of microscopic factors such as molecular order, intermolecular interactions and anharmonicity of molecular vibrations, upon other macroscopic thermo-acoustic properties of rare earth metals and reference materials.

**References**

Dugdale J S and MacDonald D K C 1953 *Phys. Rev.* **89** 832
Hartmann B 1979 *J. Acoust. Soc. Am.* **65** 1392
Moelwyn-Hughes E A 1951 *J. Phys. Chem.* **55** 1246
Narayana K L and Swamy K M 1978 *Acustica* **39** 336
Rao M R 1941 *J. Chem. Phys.* **9** 682
Reddy R R, Reddy P M and Manohara Murthy N 1987 *Acoust. Lett.* **10** 128
Sharma B K 1981 *Acustica* **48** 118, 121
——1982 *J. Phys.* **D15** 1273, 1735
——1983a *ibid* **16** 1959
——1983b *J. Acoust. Soc. India* **12** 20
——1983c *Phys. Lett.* **A95** 107
——1983d *ibid* **96** 133
——1983e *ibid* **99** 227
——1983f *J. Acoust. Soc. Am.* **73** 106
Sharma B K and Reddy R R 1984 *J. Polym. Mater.* **1** 178
——1985 *Indian J. Pure Appl. Phys.* **23** 396
Slater J C 1939 *Introduction to Chemical Physics* (New York : McGraw Hill) p 238
Soczkiewiez E 1977 *Archiv Acoust.* **2** 325
Warfied R W Hartmann B 1973 *J. Appl. Phys.* **44** 708
White G K 1973 *J. Phys. D. Appl. Phys.* **6** 2070